Transformation of dibenzothiophenes model molecules over CoMoP/Al$_2$O$_3$ catalyst in the presence of oxygenated compounds

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ABSTRACT

Decanoic acid is one of the most inhibiting compounds with CO in the transformation of the most refractory sulfur compounds in gas oils. Unlike phenols compounds, decanoic acid and CO its main by-product present a strong inhibiting effect in the conversion of sulfur compounds. The effects are due to phenomena of competitive adsorption between sulfur and oxygen compounds on the catalyst surface. Furthermore, according to oxygenated molecules, the impact on both transformation pathways (HYD and DSD) mainly involved in HDS of gas oils is not the same. Decanoic acid and CO have a greater impact on the DSD way involved in the transformation of DBT than in HYD way involved in the transformation of 46DMDBT. These results confirmed that these two reactions require two different sites located in sulfur and metal edges of the catalyst.

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1. Introduction

Biomass, and more particularly lignocellulosic materials which are available in large quantities in nature are new potential sources for the production of fuels. After the liquefaction step, which could be a pyrolysis, the bio-oil has a high content in oxygen (15–40 wt%) and could not be used directly as a gas oils due mainly to the low stability and a high corrosiveness. [1–4]. Oxygen compounds are present in various functionalities such as carboxylic acids, ketones, ethers, alcohols or phenolic compounds [4–6]. A deoxygenation process is required before using these new materials as gas oils. The deoxygenation could be carried out alone or simultaneously with the hydrodesulfurization step of crude cuts. The latest is the most economic using the HDS units existing on refinery sites. However the challenge is to transform the oxygenated compounds without modification of the performances of the conventional catalysts for the HDS of gas oils cuts to obtain gas oils with properties according the level of sulfur (10 wt ppm since 2009) imposed by the European Community (98/70/EC Directive) [7]. Otherwise, it is now well established that the sulphur compounds present in diesel fuels at sulphur levels of less than 250 wt ppm are almost exclusively substituted dibenzothiophenes, especially those in which the alkyl substituents are present in the 4 and 6 positions on the aromatic rings adjacent to the heterocycle [8–13]. That is why, dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (46DMDBT), are commonly used as models for the deep HDS of diesel fuels. Indeed, while over commonly used commercial catalysts, the transformation of DBT and 46DMDBT involved the main two reactions in HDS which are the direct C—S bond rupture (DDS way) and the hydrogenation of the aromatic ring followed by C—S bond rupture (HYD way). It is well establish in academic articles that DBT was converted mainly by the DDS way and 46DMDBT by the HYD pathway [11–16]. Many studies in the 1980s studies have reported biomass conversion. However, depending on operating conditions, the nature of the catalyst and the oxygen molecules, it is difficult to draw conclusions on mechanisms, the active sites and the impact of oxygen molecules on the transformation of sulfur compounds. More recently, new researches have highlighted the impact of oxygenates depending on the functionalities on the transformation of model sulfur compounds and on a diesel Straight-run standard. Some studies have established that these oxygenated functions are transformed under operating conditions (4.0 MPa, 340 °C) and the main oxygenated by-products are CO by decarbonylation or CO$_2$ by decarboxylation [17–21]. Only few studies [22–28] have reported the simultaneous transformation of both oxygenated molecules and sulfur molecules under HDS conditions, and even

less telling the effect of CO or CO_2 on the hydrogenation step [29,30]. Furthermore, these two articles concern the hydrodesulphurization of gasoline. Recent results showed that depending on the composition of the feed and the oxygenates, inhibiting effect were observed in the HDS performances of conventional catalysts [31,32]. Pinheiro et al. [27,30] showed that under industrial operating conditions, 2-propanol, cyclopentanone, anisole, and guaiacol, which have been found totally decompose by forming water, were not found to be inhibitors of catalytic $CoMo/Al_2O_3$ performances on the transformation of a diesel Straight-run standard. On contrary, propanoic acid and ethyldecanoate had a strong inhibiting effect on hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrogenation of aromatics (HDAr) reactions due to CO and/or CO_2 formations. They concluded that, in the range of introduced gases, inhibitions of hydrotreatment (HDT) reactions come from competitive adsorptions of CO and CO_2 with the gas oil molecule involved in HDT reactions. Moreover, these results are consistent with the hypothesis proposed in the previous work [27] which supposed that inhibitions obtained in the presence of the acid and ester compounds are due to the reaction products CO and CO_2 and not directly to the oxygenated reactants themselves. Finally, the successful treatment of oxygenated compounds into refinery processes required the limitation of the formation of inhibiting compounds by a selective catalytic liquefaction of biomass and/or by the development of a catalyst specific to selective oxygen removal, which favor the hydrogenation/hydrogenolysis reactions instead of the decarboxylation or decarbonylation reaction. The other way is to use a non sensitive catalyst at CO and or CO_2. As reported recently by Bouvier et al. [33], the $NiMo/Al_2O_3$ catalyst was less sensitive than the $CoMo/Al_2O_3$ to the presence of CO during the HDO of 2-ethylphenol a model compound of lignocellulosic materials. If we considered, the impact of oxygenates model molecules on the transformation of model sulphur compounds, Philippe and al [32] showed an inhibiting effect of phenolic compounds (guaiacol and phenol) on the HDS of DBT and 46DMDBT attributed to competitive adsorptions. However, in this case the transformation of the oxygenates is not total and the inhibiting effect is higher in the presence of guaiacol than in the presence of phenol due to a higher adsorption constant on the catalyst surface.

The present paper is focused on the effect of decanoic acid and CO and CO_2 its by-products on HDS of 46DMDBT and DBT under conditions close to deep hydrotreating of gas oils and over a $CoMoP/Al_2O_3$ catalyst and more especially on the two main DDS and HYD ways involved in HDS process. The transformation of CO and CO_2 under these experimental conditions was also investigated.

2. Experimental

2.1. Catalyst and chemicals

The catalyst was a commercial $CoMoP/Al_2O_3$ catalyst containing 4 wt% CoO, 19 wt% MoO_3 and 2.6 wt% of phosphorus. The sulfided procedure was described previously [32]. Dimethyl disulfide (>98% purity), toluene (>99% purity) were purchased from Fluka; 46DMDBT (>95% purity) from Eburon Organics and decanoic acid (>98% purity) from Alfa Aeser. They were used without further purification. Carbon monoxide and carbon dioxide (1 or 10% in mixture with H_2) have been purchased from Air Liquide.

2.2. Reaction conditions

Reaction conditions are those described in a previous paper [32]. The HDS of 46DMDBT (or DBT) with or without an oxygenated compound (guaiacol or phenol) was carried out in a fixed bed microflow reactor at 340 °C and 4.0 MPa of total pressure after an *in situ* sulfidation of the catalyst according to the procedure described above. 46DMDBT or DBT (500 ppmS) and the oxygenated compound (guaiacol or phenol: 0–5 wt% corresponding to 0–0.051 MPa of partial pressure) were dissolved in a mixture of toluene and o-xylene (used as an internal standard) to which dimethyl disulfide (DMDS) (9500 wt ppmS) was added to generate H_2S. In all cases, whatever the conversion of oxygenated and sulfur compounds, the molar balance was higher than 95% which corresponds to the experimental uncertainties.

46DMDBT or DBT and oxygenated compounds transformations were studied separately and in mixtures. The transformation of decanoic acid, CO or CO_2 alone was carried out with a partial pressure of the oxygenated compound of 0.051 MPa and H_2S partial pressure of 0.036 MPa as reported in Table 1. To examine the effect of oxygenates on the 46DMDBT or DBT transformation, the partial pressure of the latter was maintained constant at the standard 0.0019 MPa while the pressure of oxygenated compounds varied from 0.01 to 0.051 MPa. All the other partial pressures as well as the total pressure were kept constant by changing the partial pressure of the solvent (Table 1) and the ratio between the hydrogen flow rate (volume) and the reactant liquid flow rate (volume) equal to 470 NL/L. For a better precision in the activity measurements, the contact time was chosen such as to keep also the overall conversion of sulfur compounds nearly constant around 25 mol.% (24–27 mol.%) whatever the oxygenated compound content.

In order to measure the effect of the oxygenated compounds in HDS, experiments were carried out as following where various feeds were successively injected:

(1) Feed containing only one sulphur compound to obtain conversion data (around 25 mol.%) in the differential regime.
(2) Feed containing both sulphur and oxygenated compounds to measure the inhibiting effect of the oxygenated compound on the 46DMDBT or DBT transformation.
(3) Feed containing the sulphur compound alone in the same conditions as in step 1 in order to evaluate the catalyst deactivation and the modification of selectivity involved.

Global, HYD and DDS activities of the catalyst are defined as the number of moles of sulphur compounds transformed totally by the HYD way or by the DDS way per gram of catalyst and per hour.

Table 1
Partial pressure of various reactants depending of the model feed.

Feed	P_{H_2} (MPa)	$P_{oxygenates}$ (MPa)	$P_{46DMDBT}$ (MPa)	P_{H_2S} and P_{CH_4} (MPa)	$P_{toluene}$ (MPa)	$P_{o\text{-xylene}}$ (MPa)
A	2.647	0	0.019	0.036	1.246	0.0341
B	2.647	0.051	0	0.036	1.196	0.0341
C	4.0	0.01	0	0	0	0
D	2.647	0.011–0.051	0.019	0.036	1.234–1.194	0.0341
E	2.647	0.002–0.051	0.019	0.036	1.299–1.194	0.0341

T = 340 °C, P_{Total} = 4.0 MPa, H_2/HC = 470 NL/L; Feed A: 46DMDBT and dimethyl disulfide in toluene and o-xylene; Feed B: Guaiacol (or phenol) and dimethyl disulfide in toluene and o-xylene; Feed C: CO or CO_2; Feed D: 46DMDBT and oxygenates (acid decanoic) and dimethyl disulfide in toluene and o-xylene; Feed E: 46DMDBT and CO or CO_2 and dimethyl disulfide in toluene and o-xylene.
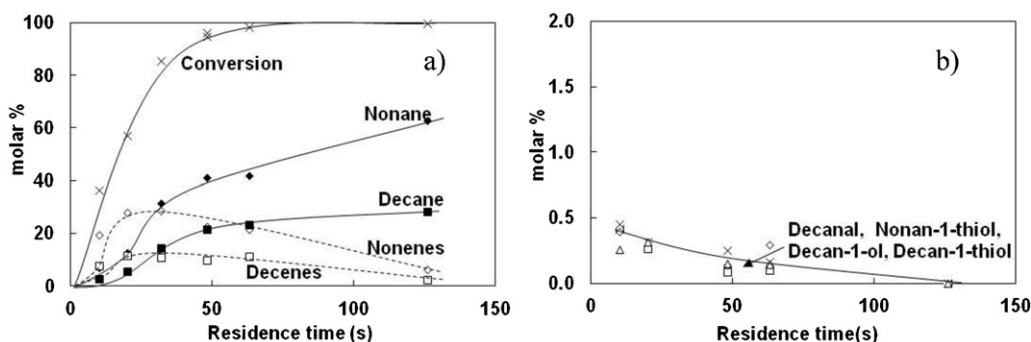
Fig. 1. Transformation of decanoic acid as function of residence time (a) conversion and main products (b) secondary products ($T = 340\,°C$, $P = 4\,MPa$, CoMoP/Al$_2$O$_3$).

The inhibition effect of the oxygenated compound in the feed was measured by the loss of activity measured by the A/A_0 ratio where A was the catalyst activity in the transformation of the sulfur compound in the presence of the oxygenated compounds and A_0 the catalyst activity in the transformation of the sulfur compound without oxygenated compounds.

2.3. Analysis of the organic compounds and of the catalyst

The reactor effluents were condensed and liquid samples were periodically collected to be analyzed by gas chromatography. The analyses were carried out with a Varian 3400 chromatograph equipped with a 25 m BP1 (SGE) capillary column (inside diameter: 0.32 mm; film thickness: 5 μm) with a temperature program from 50 to 70 °C (4 °C/min) then from 70 to 250 °C (15 °C/min). All products were identified by GC–MS (Finnigan INCOS 500) and by comparison with commercial products. CO, CO_2 and CH_4 were analyzed by gas chromatography with a Varian 450-GC equipped with an automatic sample valve, two Porapack Q columns (1 m × 1/8 in × 2 mm), a methanizer and a FID. A back-flush procedure has allowed the elimination of H_2S and all other organic compounds which could poison the methanizer Ni catalyst.

3. Results and discussion

3.1. Oxygenates transformation

The transformation of decanoic acid was studied under deep HDS experimental conditions (CoMoP/Al$_2$O$_3$, 340 °C, 4.0 MPa) and was compared to the transformation of guaicol and phenol studied previously in the same operating conditions [32]. Decanoic acid transformation leads almost exclusively to nonanes and nonenes ("C9") (deoxygenated products) obtained by decarbonylation or decarboxylation reactions and decane and decenes ("C10") obtained by hydrogenation reaction. The main products observed were nonane (C$_9$) and decane (C$_{10}$) (Fig. 1a). The formation of decenes (C$_{10}$=) and nonenes (C$_9$=) were also observed in small amount. Traces of decanal, decane-1-ol, nonan-1-thiol and decan-1-thiol were also detected and disappeared when the contact time increased. These products could be considered as primary products and the others as secondary (Fig. 1b). The C$_9$/C$_{10}$ ratio equal to two 2 shows that the decarbonylation and/or decarboxylation reactions are favored over the hydrogenation reaction. No change of the selectivity toward nonane and decane measured by the ratio between nonane and decane was noticed whatever the contact time, the formation of nonanes being majority. On the other hand, ratios between alkenes and alkanes (C$_9$ or C$_{10}$) increased with the residence time and the conversion of decanoic acid showing that alkenes were transformed in the corresponding alkanes (Fig. 2). Senol et al. [17–21] reported that in the transformation of heptanoic
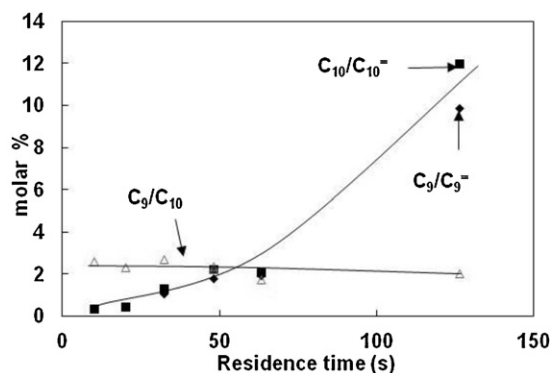
acid (1.5 MPa at 250 °C) in presence of H_2S and a CoMo/Al$_2$O$_3$ or NiMo/Al$_2$O$_3$ catalysts, hydrogenation way is the main way. Indeed, these authors reported that C_6/C_7 ratio is equal to 0.5 (calculated from the ratio of hydrocarbons to 6 carbon atoms (C$_6$) formed by the reaction decarbonylation or decarboxylation and hydrocarbons with 7 carbon atoms (C$_7$) formed by the hydrogenation reaction) for CoMo/Al$_2$O$_3$. In contrast, the main way became the decarbonylation way in the presence of a NiMo/Al$_2$O$_3$ catalyst. Senol et al. [17–21] also found very small amounts of heptanal, of heptanol, of diheptylether, heptanoate of heptyl, heptan-1-thiol and hexan-1-thiol from heptanoic acid.

The decarbonylation and/or decarboxylation of decanoic acid could also lead to the formation of CO and/or CO_2 as by-products (Fig. 3). In this case, only the formation of CO was noticed corresponding to the formation of "C$_9$" products, CO_2 was not detected. Under deep HDS operating conditions (340 °C, 4 MPa) and in the presence of a CoMoP/Al$_2$O$_3$ catalyst, the transformation of CO or

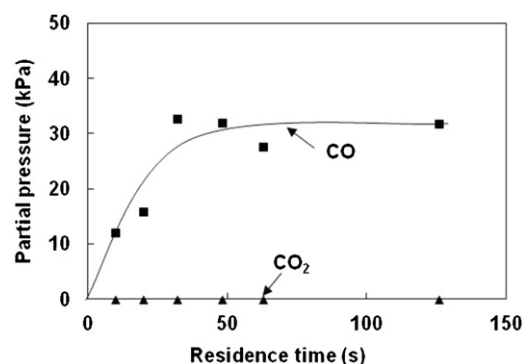**Fig. 2.** Transformation of decanoic acid: alkanes/alkenes ratios (C$_9$/C$_9$= and C$_{10}$/C$_{10}$=) and C$_9$/C$_{10}$ ratio as function of residence time ($T = 340\,°C$, $P = 4\,MPa$, CoMoP/Al$_2$O$_3$).
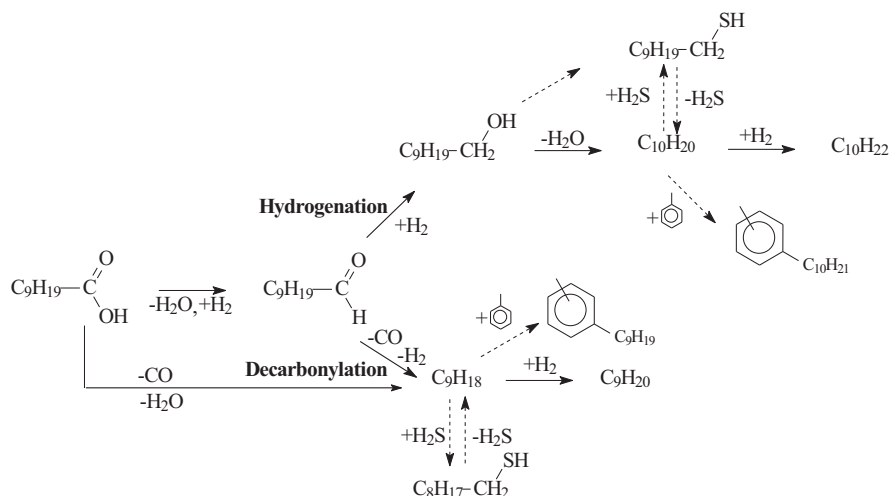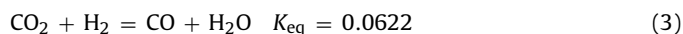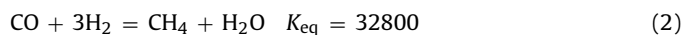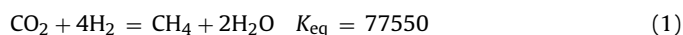

Fig. 3. Transformation of decanoic acid. CO and CO_2 formation as function of residence time ($T = 340\,°C$, $P = 4\,MPa$, CoMoP/Al$_2$O$_3$).

Scheme 1. Transformation of decanoic acid under deep HDS operating conditions ($T = 340\,°C$, $P = 4\,MPa$, $CoMoP/Al_2O_3$).

CO_2 alone was also studied in order to explain the absence of CO_2. Different reactions could be involved as reported below: methanization of CO_2 or CO (Eqs. (1) and (2)) and water gas shift reaction (3)).

$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad K_{eq} = 77550 \qquad (1)$$

$$CO + 3H_2 = CH_4 + H_2O \quad K_{eq} = 32800 \qquad (2)$$

$$CO_2 + H_2 = CO + H_2O \quad K_{eq} = 0.0622 \qquad (3)$$

Methanization reactions from CO or CO_2 are thermodynamically favored leading only to CH_4 and H_2O. The reverse water gas shift can also be observed. Under these operating conditions no transformation of CO was noticed in the presence of $CoMoP/Al_2O_3$ catalyst. In contrast, CO_2 was partially converted only into CO (34%). From this, a reaction scheme (Scheme 1) of transformation of decanoic acid could be proposed under these experimental conditions involving mainly a hydrogenation and a decarbonylation ways. Decanoic acid would be transformed into decanal by reduction which led, after hydrogenation, to decan-1-ol and then a mixture of decane and decenes by dehydration followed by hydrogenation. After the decarbonylation reaction, nonane and nonenes were produced corresponding to the main way. The third way proposed by Senol et al. [17–21] involving a direct decarboxylation of decanoic acid into nonene seems unlikely since the formation of CO_2 was never observed. Moreover, it is never completely converted under these conditions. Direct decarbonylation of the aldehyde into nonane is also limited because the selectivity measured by the ratio between alkanes and alkenes is the same for the products in "C9" and "C10" which involved the formation of nonenes. The formation of traces of nonan-1-thiol and decan-1-thiol was also observed, these compounds are in equilibrium with the corresponding alkenes. Therefore, decanoic acid scheme proposed in this paper is substantially different from that established by Senol et al. [17–21] for the transformation of heptanoic acid (which subsequently been extended to all linear acids) where a decarboxylation way was reported.

Under the same operating conditions, decanoic acid was more reactive than guaiacol and phenol (Table 2). Decanoic acid and guaiacol have a similar reactivity which is higher than the reactivity of phenol. However, decanoic acid is more reactive in HDO products than phenol and guaiacol. The HDO activity corresponds to the formation of totally deoxygenated products. As reported previously [32] guaiacol was mainly transformed into phenol which transformation was inhibited by the presence of guaiacol or catechol. These

Table 2
Comparison of the reactivity of various oxygenated compounds ($T = 340\,°C$, $P = 4\,MPa$, $CoMoP/Al_2O_3$).

	Global activity (mmol/g/h)	HDO activity (mmol/g/h)
Guaiacol	120	8
Phenol	65	65
Decanoic acid	125	125

results confirm that phenolic compounds are more refractory to the HDO than carboxylic acids.

3.2. Effect of the oxygenates on the HDS of DBT and 46DMDBT

Figs. 4 and 5 report respectively the inhibiting effect of oxygenated compounds (phenol, guaiacol, CO and decanoic acid) on the relative global activity in the transformation of 46DMDBT and DBT. An inhibiting effect of oxygenates present in low concentrations in the feed in the transformation of sulfur-containing molecules was observed. However this negative impact depends on the nature of the oxygenated compound and the sulfur compounds. Decanoic acid is the most inhibiting compound followed by CO, guaiacol and phenol. No direct effect of CO_2 was observed but depends on the amount of CO formed by the reverse reaction of water gas shift. For low partial pressures of oxygenated compounds, decanoic acid and CO have the same inhibiting effect in the 46DMDBT transformation (Fig. 4) (HYD way), guaiacol has a greater impact than phenol. For higher partial pressures (50 kPa), decanoic acid would
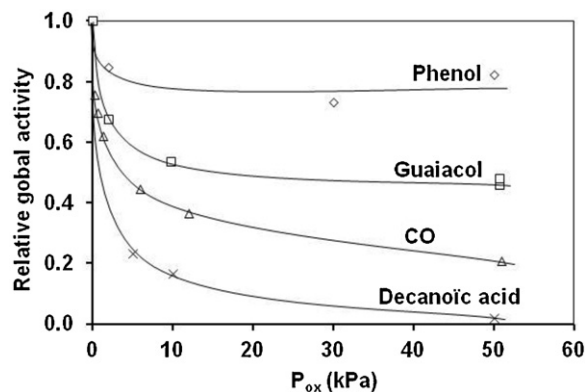

Fig. 4. Transformation of 46DMDBT: relative global activity as function of the partial pressure and the nature of the oxygenates ($T = 340\,°C$, $P = 4\,MPa$, $CoMoP/Al_2O_3$).

Table 3
Impact of decanoic acid in the transformation of DBT and 46DMDBT at different conversions of sulphur compounds ($T = 340\,°C$, $P = 4\,MPa$, CoMoP/Al$_2$O$_3$).

	DBT			46DMDBT		
Residence time (s)	3.7	22	77	16	115	306
Sulfur compounds Conv. (mol.%)						
Alone	19	70	99.5	20	85	99.6
With decanoic acid	0.5	6.6	54	3.6	38	88
Decanoic acid: Conv. (mol.%)	54.2	98.6	99.9	97.0	100	100
Decanoic acid (kPa)	22.9	0.7	0.01	1.5	0.00	0.00
CO (kPa)	19.2	34	30	31.5	29.4	35.1
Relative global activity	0.03	0.09	0.58	0.19	0.47	0.88

be more inhibitor than guaiacol and CO and especially than phenol. However, for the conversion of DBT (Fig. 5) (DSD way), an order of inhibition is clearly established, decanoic acid and CO, guaiacol and finally phenol. All these inhibiting effects could be attributed to competitive adsorption on the catalyst surface. It should be noted that the inhibiting effects measured for the oxygenated compounds are much lower than those measured for acridine under the same conditions [34]. Indeed, Rabarihoela-Rakotovao et al. [34] have shown an effect of acridine in the transformation of 46DMDBT from 20 ppm N which represents a partial pressure of 0.04 kPa of nitrogen compound. Specifically, the degree of inhibition of oxygen compounds (guaiacol, phenol and decanoic acid) is related to the nature of the oxygen function (phenol and acid) and decomposition products (H_2O, CO). As reported previously [32], guaiacol leads to a more inhibiting effect than phenol and these inhibiting effects are weaker or disappeared at higher conversions (80%) of sulfur compounds. This clearly demonstrates that the real inhibitors could be partially the oxygenated organic compounds themselves and not the water produced by decomposition. The behavior of decanoic acid is different. Its decomposition leads to the formation of hydrocarbons, CO and H_2O as by-products and the inhibiting effect is higher than in the presence of CO alone. The strong inhibiting effect of CO was also observed in the HDS of gasoline [29] and HDO of ethylphenol [33]. This effect was attributed also to a competitive adsorption between the various molecules on the catalyst surface, CO being more adsorbed as calculated by theorical approach. So decanoic acid itself is also an inhibitor. Indeed, for a partial pressure of 50 kPa of CO, there is a loss of activity of 68% in the HYD and 82% in the DSD ways. In the presence of the same partial pressure of decanoic acid, the activity loss is equal to 80% in the HYD pathway and close to 100% in the DSD way. The inhibiting effect of decanoic acid (at a constant partial pressure: 50 kPa) was measured for various conversions of DBT and 46DMDBT (Table 3) from around 20% to close 100% obtained by increasing the residence time from 3.7 to 22 s for DBT and from 16 to 306 s for 46DMDBT. This corresponds also to conversions of the decanoic acid from 54 to 100%. A decrease of the inhibiting effect of the decanoic acid in the sulfur compounds

transformation was noticed. The inhibiting effect becomes around 48% in the case of DBT and 12% in the case of 46DMDBT if only the presence of 0.01 kPa or traces of decanoic acid was considered. Indeed a relative global activity for DBT and 46DMDBT (measured by the ratio between the activity of the sulfur compound in the presence of acid decanoic and the activity of the sulfur compound alone) of 0.58 and 0.88 respectively was calculated. In fact, this inhibiting effect was not only due to the formation of CO but also of the presence of traces of decanoic acid. Indeed, the comparison of the inhibiting effect of CO alone and coming from decanoic acid shows that whatever the partial pressure of CO considered the inhibiting effect observed was higher when CO was produced by the transformation decanoic acid than this one observed when CO was introduced alone. These results clearly demonstrate that decanoic acid is also an inhibiting compound. In order to explain the difference of inhibition of CO alone and decanoic acid in the HYD and DDS ways, it is necessary to consider both the difference in structure of sulfur-containing molecules and morphology of the catalyst under these operating conditions and therefore the nature of active sites described by Krebs et al. [35]. The actives sites were located at metal edges and sulfur edges of slabs of MoS$_2$ where cobalt was in substitution of molybdene in 100% in the sulfur edge and only 50% cobalt in metal edge. In the same way it is possible to consider two kinds of sites which could be sulfur vacancies located in metal and sulfur edges. In this case, CO and the decanoic acid could be adsorbed both. However, as reported in the literature [14] the transformation of DBT which involved mainly direct C—S bond rupture could be carried out both edges (metal and sulfur). In contrast, 46DMDBT which involved mainly HYD pathway, due to steric hindrance, could be carried in metal edge or as proposed recently on the fully sulfided Mo edges containing no coordinatively unsaturated sites (called brim site) [16,36–38]. Indeed, the sulfur vacancies are not required for the flat adsorption of the reactant involved in these reactions [16]. Consequently, the DBT transformation was more inhibited than 46DMDBT by the presence of decanoic acid or CO.

4. Conclusion

The presence of oxygenated molecules whatever their functionality (phenols, acid or CO) inhibits the transformation of sulfur compounds. Nevertheless, the negative effect depends on the oxygen and the sulfur-containing molecule. Thus, decanoic acid is more inhibitor than CO, guaiacol and phenol. The effects are due to phenomena of competitive adsorption between sulfur and oxygen compounds on the catalyst surface. Furthermore, according to oxygenated molecule, the impact on both transformation pathways (HYD and DSD) mainly involved in HDS of gas oils is not the same. Decanoic acid and CO (decomposition product of the acid) have a greater impact on the way to DSD conversion of DBT. As previously showed, phenol, the less inhibitor compound, has a similar effect on both way, unlike guaiacol which would cause a greater inhibition so partially and irreversibly on HYD. This inhibition is attributed to a carbon deposition. Thus, molecules from simple models of a
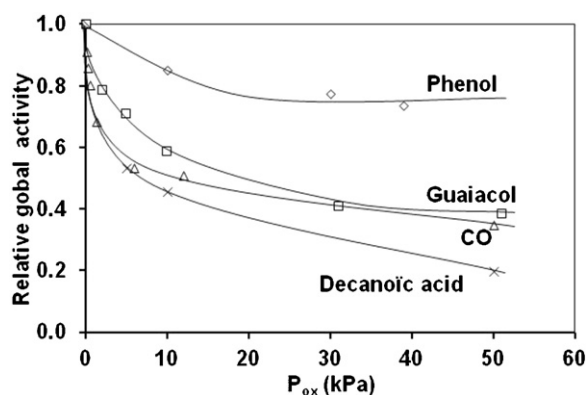

Fig. 5. Transformation of DBT: relative global activity as function of the partial pressure and the nature of the oxygenates ($T = 340\,°C$, $P = 4\,MPa$, CoMoP/Al$_2$O$_3$).

representative bio-oil, it could be possible to establish the types of oxygen functions that would be most inhibitors. Indeed, only the molecules leading to the formation of H_2O as a by-product oxygenate such as phenols or guaicol should have a limited effect on the HDS of a diesel. However, these molecules appear to lead to the formation of coke. In contrast, oxygen compounds producing CO molecules during their deoxygenation, such as carboxylic acids, have a greater effect on the HDS of diesel fuel, mainly on direct C—S bond rupture. It therefore seems important to adapt the catalyst properties to the feed which must to be hydrotreated. Indeed, recent results showed that, under hydrodeoxygenation (HDO) conditions, $NiMo/Al_2O_3$ and Mo/Al_2O_3 catalysts are much less sensitive to the presence of CO than $CoMo/Al_2O_3$ catalyst.

Acknowledgements

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